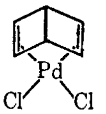
Although the second dibromide was too unstable to permit purification, the nmr spectrum of the original mixture clearly revealed the presence of this component [τ 2.97 (triplet; $J = 2$ cps), 5.60 (singlet), 6.82 (triplet; $J = 2$ cps); integrated ratio 1:1:1], apparently the *cis*-dibromide IVb (*cis*:*trans* ratio 30:70, by nmr). This assignment was supported by the results of an ozonization–hydrogenolysis sequence, as above, but carried out on the dibromide mixture; dicarboxylate ester VI was found in an amount (61%) not greatly different from that secured (67%) from the pure *trans* case.[9] Furthermore, the mass spectra (molecular ion m/e 238) of IVa and the *cis–trans* mixture were essentially identical.

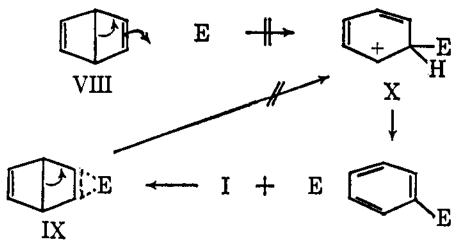
Excess osmium tetroxide in ether at room temperature converted "Dewar benzene" to a tetrol, mp 184–186°; nmr data: broad singlets at τ 5.25, 5.97, 7.72, all in the integrated ratio of 2:2:1; the low-field signal at τ 5.25 disappears under deuterium-exchange conditions; strongly periodate positive. The oxidation product revealed the following mass spectral behavior: molecular ion m/e 146 (weak), 128, 110, 99, 86, 73 (base peak), 60, 57, 55, 53, 45. In the reaction system, osmium tetroxide neither detectably isomerized I to benzene nor converted it to phenol.

A relatively stable metal coordination complex (VII) of "Dewar benzene" was prepared by interaction of the hydrocarbon with bis(benzonitrile)palladium dichloride in methylene dichloride.[10] Precipitating from the reaction solution, the light brown amorphous solid exhibited infrared behavior (7.18, 7.97, 8.51, 10.05 μ) consonant with the assigned structure. As in the norbornadiene–rhodium(I) acetylacetonate case,[11] the olefinic protons are shifted in the nmr spectrum to the higher field position of the methine hydrogens (τ 5.60 (broad singlet)). While the reaction mixture was being observed by nmr means, the displacement of hydrocarbon ligand by pyridine-d_5 was carried out; bicyclohexadiene was released, but no detectable amount of Kekulé benzene was generated. The above data preclude the structural possibility benzene–palladium dichloride, which in fact remains unknown.



VII

On the basis of the above examples, an olefinic bond in "Dewar benzene" is prone to interact with an electron-deficient species while retaining a cyclobutene unit, despite the availability of an aromatization pathway (VIII or IX → X) involving an isomerization of the well-recognized cyclobutyl → homoallyl cation type.



It thus appears that the orbital symmetry factors which inhibit nonphotochemical conversion of "Dewar benzene" to Kekule benzene[2a] can operate as well in the transition state of a reaction with an external agent.

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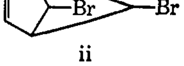
[9] There was detected also a 0.7% yield of acid which was indistinguishable (by vpc on the diester) from cyclobutane-*cis*-1,3-dicarboxylic acid.[8] This tentatively identified substance may find its origin in small amounts of the abnormal bromination product ii.



ii

[10] A close precedent is the formation of an olefin complex from palladium dichloride and norbornadiene: R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82**, 535 (1960).

[11] Observation made in this laboratory.

Photolytic Production of Hydrated Electrons from Aqueous Potassium Octacyanomolybdate(IV) and Potassium Octacyanotungstate(IV)

Sir:

We wish to report some observations on the flash photolysis of aqueous potassium octacyanomolybdate(IV), $K_4[Mo(CN)_8]\cdot 2H_2O$, and potassium octacyanotungstate(IV), $K_4[W(CN)_8]\cdot 2H_2O$. The investigation was prompted by recent observations[1-4] that photoelectron production occurs with aqueous ferrocyanide ion plus some considerations as to what desirable properties one should look for in searching for other complex cyanides that might behave similarly. The prerequisites assumed were that (a) the wavelength region illuminated by a conventional flash system should contain absorption bands of a charge-transfer character, (b) there be a reasonably stable complex of the same stoichiometry and one higher oxidation state, and (c) that there be no stable complex of the same stoichiometry and one lower oxidation state (so that electron scavenging would not be important). The above octacyanides meet these criteria admirably; both show fairly intense adsorption features in the near ultraviolet,[5] the oxidation potentials to the corresponding V valence state compounds are 0.84 and 0.57 v for $Mo(CN)_8^{-4}$ and $W(CN)_8^{-4}$, respectively,[6] and no III valence-state octacyanides are known. Only the complex $K_4[Mo(CN)_7]\cdot 2H_2O$ has been reported,[7] and it is dubious whether the molybdenum(III) octacyanide

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exists at all because the formal electron count on the molybdenum would exceed the next rare gas number of electrons. It is for the same reason, presumably, that $Co(CN)_5^{-3}$ but not $Co(CN)_6^{-4}$ is known.[8]

The solutions of $Mo(CN)_8^{-4}$ and $W(CN)_8^{-4}$ were photolyzed in a 1.5-cm by 15-cm quartz cell mounted parallel to two krypton-filled flash tubes giving 600 joules per flash. Transients were observed by following the intensity of a monotoring light beam, directed longitudinally through the cell, by means of a photomultiplier–oscilloscope combination. The light was monochromatized to 680 mμ by means of interference and glass-blocking filters. The water used was commercially triply distilled and further purified by distillation and by passing the vapor, along with oxygen gas, through a Vycor tube heated to 850° to remove organic impurities. The concentrations of dissolved oxygen and of carbon dioxide were reduced to a tolerable level with respect to electron scavenging[9] by means of repeated freeze–thaw cycles.

On flashing deaerated solutions of 10^{-4} *M* $Mo(CN)_8^{-4}$ or 10^{-4} *M* $W(CN)_8^{-4}$, a transient was observed over a period of about 40 μsec; for a 2×10^{-4} *M* solution of $Mo(CN)_8^{-4}$, the initial change in absorption on flashing was less, and the decay rate of the transient was greater than that associated with the more dilute solution. No transient could be seen when aerated solutions of these complexes were flashed. Essentially the same behavior was found for 2×10^{-4} *M* $Fe(CN)_6^{-4}$; the transient absorption was somewhat greater and the decay rate longer, about 90 μsec, than for the octacyanides.

As in the flash photolysis experiments of Matheson, *et al.*,[1] $Fe(CN)_6^{-3}$ was identified spectrally as a final product. From the concentration of $Fe(CN)_6^{-3}$ and the estimated value of the optical density of the transient, the molar extinction coefficient was *ca.* 10^4 M^{-1} cm^{-1}; a species absorbing so intensely at 680 mμ can reasonably be identified as e_{aq}^-.[10] Furthermore, the decay period of *ca.* 90 μsec in the case of ferrocyanide is similar to that of 70 μsec reported by Matheson, *et al.*[1] The quite parallel behavior of the transient observed with $Mo(CN)_8^{-4}$ and $W(CN)_8^{-4}$ again justifies identifying it as e_{aq}^-; this assignment is confirmed and instrument artifact ruled out by the complete absence of the transient in all cases for aerated solutions.

In the case of octacyanides, the lifetime will depend on the scavenging rate of the parent and product complexes (and on any impurities present), but, from the effect of doubling the $Mo(CN)_8^{-4}$ concentration, it appears that e_{aq}^- was disappearing mainly by reaction with the parent complex. Bimolecular rate constants for the reaction of cyano complexes with e_{aq}^- are in the range of 10^8–10^{10} M^{-1} sec^{-1},[11–14] and if a *k* value of 10^9 M^{-1} sec^{-1} is taken for $Mo(CN)_8^{-4}$, the half-life for e_{aq}^- should be about 9 μsec, or about what was observed.

Returning to the general results, the approximate yield of e_{aq}^- was in order $Fe(CN)_6^{-4} > W(CN)_8^{-4} > Mo(CN)_8^{-4}$. It might be noted that this is also the order of increasing oxidation potential.

Although the products of the photolyzed octacyanides have not yet been identified, both the aerated and the deaerated solutions exhibited a faint pink color (*vide infra*) on flashing. If the photolysis cell was encased in a Pyrex glass sleeve, opaque to light below 280 mμ, no transient was observed, but the absorbed intensity was now about one-tenth of that previously, so this experiment was not conclusive in regard to electron production at longer wavelengths. Higher concentrations could not be used because of the previous indication that the transient would then be scavenged too efficiently to be seen in any event.

While the occurrence of photoelectron production with these octacyanides is of interest in itself, an added aspect is that the observation may lead to some better understanding of their general photochemistry. Both $Mo(CN)_8^{-4}$ and $W(CN)_8^{-4}$ are known to be photosensitive;[5,15–17] the former complex has been the more studied and appears eventually to go to an aquotetracyano product. A transient red species, of several minutes' life and of uncertain nature, has been observed, however, and there is now the possibility that the production of this species may in some way be connected with that of the molybdenum(V) octacyanide and photoelectrons. A similar complexity exists in the case of $Fe(CN)_6^{-4}$; with light of wavelength less than 300 mμ, the results of both flash photolysis[1] and competition studies[2–4] indicate that the primary mode of reaction is the formation of e_{aq}^- and $Fe(CN)_6^{-3}$, attributed to a charge-transfer band situated at 255 mμ.[2] At wavelengths greater than 300 mμ, the principal photochemical reaction of $Fe(CN)_6^{-4}$ appears to be the aquation to form $Fe(CN)_5(H_2O)^{-3}$.[4,18,19]

Since the 250-mμ bands of $Mo(CN)_8^{-4}$ and $W(CN)_8^{-4}$ are of a charge-transfer character,[16,20] the possibility exists that there may be a complete parallel with the $Fe(CN)_6^{-4}$ system with e_{aq}^- production restricted to the short-wavelength band and photoaquation to the longer wavelength ones. However, our present results do not preclude the possibility that the two processes may occur together and over a wide wavelength region. Experiments are now in progress to determine the extent of e_{aq}^- production at longer wavelengths. The results may lead to a resolution of some current conflicts in the interpretation of the general photolysis behavior of these octacyanides.

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